Determining the ages of comets from the fraction of crystalline dust

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The timescale for the accretion of bodies in the disk surrounding a young star depends upon a number of assumptions, but there are few observational constraints. In our own Solar System, measurements of meteoritic components can provide information about the inner regions of the nebula, but not the outer parts. Observations of the evolution of more massive protostellar systems (Herbig A_e/B_e stars) imply that significant changes occur in the physical properties of their dust with time[1]. The simplest explanation is that thermal annealing of the original, amorphous grains in the hot inner nebula slowly increases the fractional abundance of crystalline material over time. Crystalline dust is then transported outward, where it is incorporated into comets that serve as a long-term reservoir for dust disks, such as that surrounding Beta Pictoris. Here we show that when applied to our own Solar System, this process can explain observed variations in both the volatile and dusty components of comets, while also providing a natural indicator of a comet's mean formation age. Studies of comets with different dust contents can therefore be used to investigate the timescales of the early Solar System.

Since the first observations of the dust disk around Beta Pictoris (a relatively old protostellar A star), it has been recognized[2] that these disks are unstable to radiative forces and are replenished from larger bodies such as comets. The mid-infrared spectrum of grains around Beta Pictoris[3] is consistent with dust observed in Comet Halley and attributed to crystalline olivine[4,5]. In addition, the mid-infrared spectra of Herbig A_e/B_e stars without companions evolve from those of amorphous astronomical silicate[6] to spectra consistent with crystalline olivine as a function of increasing age[1]. Observation of amorphous grains in the youngest systems eliminates the protostellar accretion shock as the source of crystalline minerals in these stars. Thermal annealing of amorphous, originally interstellar, grains in the inner regions of these nebulae provides a natural explanation for the observation of crystalline grains in dust disks and in comets if annealed dust can be transported to regions where comets might form.

Blue-shifted winds extending for more than a thousand astronomical units (AU) are often observed above and below the disks of Herbig A_e/B_e stars viewed edge-on (C. A. Grady, personal communication). Several authors[7,8] have discussed the likelihood of outward mixing in a nebular environment. Outward mixing might occur by material exchange between adjacent turbulent convection cells within the disk[8]. Such a situation would provide a lower limit to the outward flux of nebular material. A more interesting suggestion is that larger-scale vortices resulting from non-linear momentum terms that are often neglected in nebular models would cause a higher rate of outward material flow in the disk[8]. Both mechanisms should work to some extent over the lifetime of the nebula, but one might easily expect the rate of outward transport to vary over time. Although the rate of outward mixing and the potential variation of this rate with time will determine the exact ratio of crystalline-to-total dust in the nebula, the increase in crystalline dust in the outer nebula should be monotonic.

The rate of spectral change in initially amorphous magnesium silicate smokes is extremely sensitive to annealing temperature[9]. Recent laboratory studies allow prediction of the mid-infrared spectrum of magnesium silicate dust based on its time–temperature history[10]. The time required for silicate grains to anneal to crystalline olivine at 1,000 K is of the order of a few hundred days. This same transition occurs in about an hour at 1,050 K, yet requires centuries at 950 K and eons at 850 K (Table 1). Dust in comets comes in at least two varieties[11,12], crystalline and amorphous. Although amorphous dust could have been incorporated directly into growing comets, comets could not have formed under conditions that produced crystalline grains, nor could they survive the temperatures required to crystallize amorphous grains *in situ* during a previous perihelion passage. However, the temperatures required to crystallize the amorphous silicates observed in comets are found in the innermost regions of the solar nebula[13].

Models of cometary chemistry[14,15] have always had difficulty explaining the observed ratio of interstellar molecules[16] (such as CO, N_2) to molecules produced in the solar nebula. Formation of these more complex materials—for example, hydrocarbons, ammonia, and so on—requires higher pressures and temperatures than those found in nebular models for regions beyond the orbits of Jupiter or Saturn. A mixture of nebular products with those produced sporadically in giant gaseous protoplanets has often been invoked to explain the observed ratios. Cycling just a small fraction of nebular gas and dust from the higher-pressure, higher-temperature inner nebula could offer a simple alternative explanation for the more complex, volatile chemistry of comets. However, operation of this transport mechanism throughout much of the history of the nebula would result in some very specific correlations between the chemistry of comets and the mid-infrared spectra of their dust, provided that comets form on timescales significantly shorter than the lifetime of the solar nebula.

The formation of comets in a minimum-mass nebula has been examined using an enhanced, one-dimensional model[17] to follow the accretion of micrometre-size dust particles into kilometre-scale bodies. Comets form on a timescale of a few hundred thousand years, even neglecting several factors that might result in faster accretion rates. This model indicates that a growing comet accretes material from a large volume in the nebula, as the initial coagulation process is aided greatly by gas-drag-induced orbital migration. This migration homogenizes the material accreted into comets by giving them feeding zones from 10 to 100 AU in radius and could obscure small compositional differences in comets ending the accumulation phase at different nebular radii. Comets would form much more rapidly in a higher-mass nebula where gas-drag-induced orbital migration and accumulation due to gravitational instabilities would both be more important processes. The extent of the differences we might expect to observe in the dust content and in the chemical compositions of individual comets is dependent on the ratio of the comet accumulation timescale to the nebular lifetime. If these timescales are comparable, then all comets should look fairly similar. If the nebular lifetime were much longer than the time required to accumulate comets then we would predict substantial diversity in this population as the crystalline fraction of the dust and the complex organic content of the volatiles increases with time. These latter predictions certainly appear to be more consistent with observations of both the dust[11,12] or gas[18,19] content of recent comets.

Comets that formed very early in the history of the solar nebula will consist almost exclusively of amorphous silicates and unaltered

Table 1 Experimentally measured (and extrapolated) annealing times

Annealing temperature (K)	Time to crystallization (s)
1,100	1.9×10^{0}
1,050	4.1×10^{3}
1,000	1.9×10^{7}
950	2.2×10^{11}
900	7.1×10^{15}
850	7.7×10^{20}

interstellar ices since no processed material is yet available. The average comet formed late in nebular history will contain more hydrocarbons, ammonia and annealed dust than one formed earlier. We do not suggest that this increase will necessarily be linear; but, after accretion of fresh material from the surrounding molecular cloud ceases, the accumulation of processed gas and dust in the region of comet formation should at least be monotonic with time. The time-dependent nature of the dust and gas accreted into comets might easily obscure less significant differences in cometary chemistry—such as the potential distinction between comets accreted at 'higher' temperature in the Jupiter–Saturn region from those accreted in cooler zones near, or even beyond, the Uranus–Neptune region.

Older comets should be rich in CO, CO_2 and N_2 and amorphous dust while younger comets should contain an abundance of crystalline olivine, hydrocarbons, ammonia and other essential prebiotic compounds. Specifically, we predict that the fraction of crystalline dust is correlated to the ratios of hydrocarbons to CO and of ammonia/amines/amides to N_2. Figure 1 shows the vapour pressures[20,21] of a variety of simple compounds including both interstellar grain components such as N_2, CO and CO_2, and more hydrogenated species that were synthesized in the nebula, for example, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8 and NH_3. It is clear that interstellar grains heated to above 50 K in the nebula will lose CO and N_2 from their mantles, whereas interstellar CO_2 could remain trapped. (The formation of clathrates in larger aggregates or the trapping of volatile gas in void spaces could preserve larger quantities of CO or N_2 than might otherwise be predicted by our simple model.) Hence CO and N_2 are both suitable indicators of interstellar volatiles in comets. Alternatively, if ammonia and most hydrocarbons synthesized in the nebula are cooled to below 150 K, they will be trapped on grain surfaces. CH_4 requires much cooler temperatures to achieve the same degree of condensation and might not condense into comets even if it were present in the nebula. Therefore CH_4 would not make a useful indicator of processed nebular gas in comets. A good proxy for the ratio of processed-to-primitive nebular gas in comets would be the ratio of C_2H_4 to CO and another would be the ratio of C_2H_6 to CO. The hydrocarbons represent materials synthesized primarily in the nebula and then trapped on icy grains, whereas CO is associated with grain mantles formed within a giant molecular cloud core that has never been sufficiently heated to vaporize. Using similar reasoning, the ratio of NH_3 to N_2 should also be a good measure of the ratio of processed-to-primitive gas in comets. Hence, we predict that the ratio of crystalline-to-total cometary dust will be positively correlated to the ratios of C_2H_4/CO, C_2H_6/CO and NH_3/N_2 in cometary comae.

An ability to sequence comets according to their relative ages would be a useful tool in understanding a number of events in the primitive solar nebula. For example, the question of whether Jupiter formed early in the history of the nebula might be answered by comparison of the 'age' distribution of Oort-cloud comets versus the relative ages of comets in the Kuiper belt. Because Kuiper-belt comets formed in place they should show a wide variety of ages, whereas Oort-cloud comets might not include any of the most primitive (oldest) comets if the giant planets formed very late in nebular history. A measure of the relative accumulation age of individual comets would also provide an interesting discriminator for use in choosing targets for space flight missions. Sample returns from comets of various ages could be dated to yield the lifetime of the solar nebula. Missions to 'old' comets would return interstellar ices and primitive grains, whereas missions to younger comets would yield information on chemical processes in the nebula and the formation of biogenic molecules essential for the chemical evolution of life in the Solar System. Finally, the observed diversity in the chemical composition of comets could help to constrain the timescale for the formation of individual comets, compared to the lifetime of the nebula. This, in turn, could be used to provide new constraints on the mass of the solar nebula necessary to form comets at the requisite rate. □

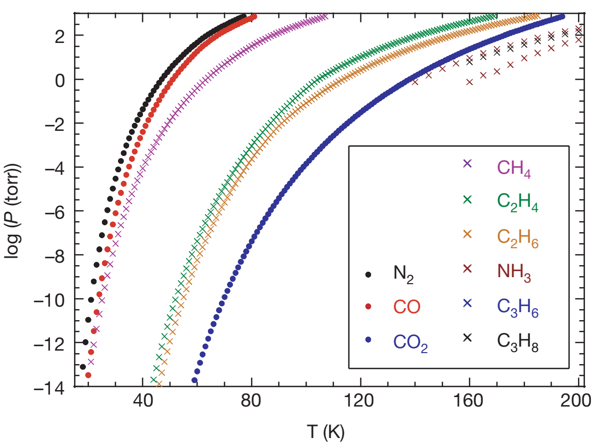

Figure 1 Vapour pressures in the range 25–200 K for a selection of simple compounds based on refs 20 and 21. The compounds include both interstellar grain mantle components (N_2, CO, CO_2) and more hydrogenated species that were almost certainly formed in the nebula (CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, NH_3) at relatively high pressures and temperatures.

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1. Grady, C. A. *et al. Protostars and Planets IV* (eds Mannings, V., Boss, A. P. & Russell, S. S.) 613–638 (Univ. Arizona Press, Tucson, 1999).
2. Smith, B. A. & Terrile, R. J. A circumstellar disk around β Pictoris. *Science* **226,** 1421–1424 (1984).
3. Knacke, R. F. *et al.* The silicates in the disk of β Pictoris. *Astrophys. J.,* **418,** 440–450 (1993).
4. Campins, H. & Ryan, E. V. The identification of crystalline olivine in cometary silicates. *Astrophys. J.* **341,** 1059–1066 (1989).
5. Ryan, E. V. & Campins, H. Comet Halley: Spatial and temporal variability of the silicate emission feature. *Astron. J.* **101,** 695–701 (1991).
6. Draine, B. T. & Lee, H. M. Optical properties of interstellar graphite and silicate grains. *Astrophys. J.* **285,** 89–108 (1984).
7. Prinn, R. G. On neglect of non-linear momentum terms in solar nebula accretion disk models. *Astrophys. J.* **348,** 725–729 (1990).
8. Stevenson, D. J. Chemical heterogeneity and imperfect mixing in the solar nebula. *Astrophys. J.* **348,** 730–737 (1990).
9. Hallenbeck, S. L., Nuth, J. A. & Daukantas, P. L. Mid-infrared spectral evolution of amorphous magnesium silicate smokes annealed in vacuum: Comparison to cometary spectra. *Icarus*
10. Hallenbeck, S. L., Nuth, J. A. & Nelson, R. N. Evolving optical properties of annealing silicate grains: From amorphous condensate to crystalline mineral. *Astrophys. J.* **535,** 247–255 (2000).
11. Hanner, M. H. The silicate material in comets. *Space Sci. Rev.* **90,** 99–108 (2000).
12. Hanner, M. H., Lynch, D. K. & Russell, R. W. The 8–13 micron spectra of comets and the composition of silicate grains. *Astrophys. J.* **425,** 274–285 (1994).
13. Woolum, D. S. & Cassen, P. Astronomical constraints on nebular temperatures: Implications for planetesimal formation. *Meteor. Planet. Sci.* **34,** 897–907 (1999).
14. Prinn, R. G. & Fegley, B. in *Origin and Evolution of Planetary and Satellite Atmospheres* (eds Atreya, S. K., Pollock, J. B. & Matthews,M. S.) 78–136 (Univ. Arizona Press, Tucson, 1989).
15. Fegley, B. in *The Chemistry of Life's Origins* (eds Greenberg, J. M., Mendoza-Gomez, C. X. & Pirronello, V.) 75–147 (Kluwer, Dordrecht, 1993).
16. Gerakines, P. A. *et al.*Observations of solid carbon dioxide in molecular clouds with the Infrared Space Observatory. *Astrophys. J.* **522,** 357–377 (1999).
17. Weidenschilling, S. J. The origin of comets in the solar nebula: a unified model. *Icarus* **127,** 290–306 (1997).
18. A'Hearn, M. F., Millis, R. L., Schleicher, D. G., Osip, D. J. & Birth, P. V. The ensemble properties of comets: results from narrowband photometry of 85 comets, 1976–1992. *Icarus* **118,** 223–270 (1995).
19. Mumma, M., Weissman, P. & Stern, S. A. in *Protostars and Planets III* (eds Levy, E. & Lunine, J.) 1177–1252 (Univ. Arizona Press, Tucson, 1993).
20. Brown, G. N. & Ziegler, W. T. in *Advances in Cryogenic Engineering* Vol. 25 (eds Timmerhaus, K. D. & Snyder, H. A.) 662–670 (Plenum, New York, 1980).
21. Lide, David R. Lide (ed.) *CRC Handbook of Chemistry and Physics: 75th edn* Section 6, 66–76 (CRC Press, Boca Raton, 1994).

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